

===== WPI =====

- TI - Additives for paper-making giving good tensile strength on drying - contg. graft copolymer prepd. by polymerisation of acryl amide and/or methacryl amide, anionic vinyl monomer and crosslinking vinyl monomer.
- AB - J07109691 Additives for paper-making contain a graft polymer as the effective components. The polymer is prepared by polymerising monomer mixture consisting of (a) acrylamide and/or methacrylamide, (b) anionic vinyl monomer and (c) a crosslinking vinyl monomer in an aq. soln. contg. cationic starch.
- ADVANTAGE - The additives impart paper with good tensile strength on drying and various strength in paper layer and tear strength, etc..
 - In example, a monomer mixture also contains (d) cationic vinyl monomer. The polymer is prepared by polymerising 80-20 pts. of monomer mixture contg. 40-98.5 mol% of (a), 2-30.0 mol % of (b), 0.02-10 mol % of (C) and 0-20.0 mol % of cpd. (d), in the aq. soln. contg. 20-80 pts. wt. of a cationic starch.
 - Mixt. of 150 g aq. soln. of 18 % cationic tapioca starch, 60 g 40 % acrylamide, 3.4 g 80% acrylic acid and 150 g water were mixed, adjusted to a pH value of 4.0 and added 0.4 g N,N-dimethylacrylamide. Added the mixture was added 2.7 ml aq. 2% ammonium persulphate and 2.7 ml aq. 2% Na bisulphite soln. and the mixture was reacted at 60-80 deg.C for 3 hrs. to give a graft polymer. The polymer was reacted with 4.4 g aq. 10 % ammonium persulphate at 70-80 deg.C for 4 hrs. and then added 80 g water, followed by adjusting to a pH value of 6.4 to give an amphoteric graft starch polymer. The polymer had a solid content of 12.0 % and had a viscosity of 2600 cps. at 25 deg.C. (Dwg. 0/0)
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- JP7109691 A 19950425 DW199525 D21H17/28 006pp
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===== PAJ =====

- TI - ADDITIVE FOR PAPER MANUFACTURING
- AB - PURPOSE: To obtain an additive improving the tensile strength and intralayer strength of paper in its drying, also presenting excellent effect in terms of tear strength.
- CONSTITUTION: This additive for paper manufacturing contains, as active ingredient, a graft polymer produced by polymerizing, a monomer mixture composed of an acrylamide and/or methacrylamide, an anionic vinyl monomer, a crosslinkable vinyl monomer and, as necessary, a cationic vinyl monomer in an aqueous solution containing cationic starch.
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- PA - SEIKO KAGAKU KOGYO CO LTD
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* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the additive for paper manufacture which is related with the additive for paper manufacture, and has the outstanding tensile strength at the time of dryness of paper in more detail, and can be enough satisfied also about many intensity and tear strength, such as intensity in paper.

[0002]

[Description of the Prior Art] It sets like a paper maker and various kinds of additives for paper manufacture are used from the former for the purpose which improves quality of paper. For example, denaturation starch, such as cation nature starch, pregelatinization starch, and an oxidized starch, or acrylamide system polymer and its derivative, the polyamide polyamine EPIKUROHI drine compounds resin, the melamine, the formaldehyde resin, etc. are used according to the purpose demanded.

[0003] Although denaturation starch is cheap, since the paper durability enhancing effect per amount used is poor, and it must be used so much and it is moreover necessary to carry out the cooking dissolution before use, recently, instead of this, from workability and the performance side, the additive of a synthetic macromolecule is fond and is used. The typical thing of a synthetic-macromolecule additive is acrylamide system polymer, and has the cation nature (amphoteric) acrylamide system copolymer which copolymerizes the Mannich-reaction object of anionic acrylamide system polymer and a polyacrylamide and the cation nature (amphoteric) acrylamide system polymer obtained by the Hofmann degradation reaction or (meta) an acrylamide, an anionic vinyl monomer, and a cation nature vinyl monomer.

[0004] While acrylamide system polymer has the performance which was excellent as a dryness paper durability agent, since it is expensive, the use is receiving restrictions economically.

[0005] The additive which had each property of acrylamide system polymer and a starch system additive is also known for this industry. For example, the additive for paper manufacture which comes to carry out the polymerization of the unsaturated carboxylic acid to an unsaturation amide by water-dispersion polysaccharide's existence-ization is taught to JP,38-17051,B. Moreover, the paper reinforcing agent which consists of copolymer mixture [****] which uses as a main monomer component the graft starch polymerization acrylamide which carried out the polymerization of an acrylamide and the unsaturated carboxylic acid to the bottom of the existence of at least a kind of water-soluble water-dispersion polysaccharide and its derivative is taught to JP,50-12481,B. In addition, the paper reinforcing agent which carried out the polymerization of a dialkyl (meta) acrylamide, an acrylic acid (meta), and (meta) the monomer mixture of an acrylamide in the solution of starch is also indicated by JP,63-29696,A.

[0006] The additive for paper manufacture which can also improve tear strength is indicated at the same time the graft starch polymer obtained by carrying out the polymerization of the monomer which consists of an acrylamide (meta), an alpha.beta-unsaturated carboxylic acid (salt), or hydroxy (meta) acrylate into cation nature polysaccharide solution to JP,2-26994,A and JP,4-50395,A further again reinforces tensile strength and the intensity in a layer.

[0007]

[Problem(s) to be Solved by the Invention] Although many general intensity is required of paper of course, tear strength is the important requirements for paper. For example, a tearing strength is required of tensile strength especially strong against the paper used for kraft paper, a craft adhesive tape, etc., and the after-mentioned on-the-strength row in a layer.

[0008] Although the above-mentioned acrylamide system paper reinforcing agent is effective in raising the intensity at the time of dryness of paper, there is a fault in which a tearing strength is reduced. On the other hand, although a starch system paper reinforcing agent does not reduce tear strength like an acrylamide system paper reinforcing agent, since it is deficient in the effect of increasing many general intensity, it has the difficulty that it must be used so much. Moreover, in addition to the fault in which tear strength is reduced, a polyamide polyamine-EPIKUROHI drine compounds resin, a melamine, a formaldehyde resin, etc. have the defect which makes disaggregation of a maculature difficult. On the other hand, the additive for paper manufacture indicated by said JP,2-26994,A and the 4-50395 official report has few degrees to which many general intensity of paper is raised and tear strength is moreover reduced. However, a satisfying result cannot necessarily be got in that many intensity, such as tensile strength and intensity in a layer, is made to strengthen, but it has still left the room of improvement.

[0009] Especially this invention aims at offering the new additive for paper manufacture which can manufacture the paper which can be enough satisfied also in respect of a tearing strength while it improves the tensile strength at the time of dryness, and the intensity in a layer.

[0010] The intensity in a layer said to this invention shows the strength in the thickness direction of paper, and has the bonding strength between fiber, and the close relation. this -- edited by Japan Technical Association of the Pulp and Paper Industry -- since it was indicated by the "kind [of paper pulp], and examining method" 248 page, in this invention, the intensity in a layer was measured in this writing based on the "measuring method by the tensile-strength testing machine" of a publication Hereafter, it sketches about the measuring method.

[0011] As shown in drawing 1 , it sticks so that an adhesive tape may be stuck to both sides of a test piece, next, the ends of an adhesive tape are mutually pulled apart, as shown in drawing, and it is made T typeface, and fixes to a vertical grip of a light-load tension tester, and the highest load when exfoliating fixed distance in a low speed (a part for 50-100mm/) is measured.

[0012]

[Drawing 1]

[Means for Solving the Problem] The polymerization object which this invention persons make carry out out the graft polymerization of the vinyl monomer [****] into the solution containing cation nature starch as a result of repeating research wholeheartedly aiming at improvement of the additive for graft starch polymerization system paper manufacture, and is obtained found out the new additive for paper manufacture and new bird clapper which can attain the desired end.

[0013] That is, this invention tends to offer the additive for paper manufacture which contains the graft polymerization object obtained by carrying out the polymerization of the monomer mixture which consists of a cation nature vinyl monomer the (a) acrylamide and/or if needed [meta-(acrylamide b) anionic vinyl (monomer c) cross-linking vinyl monomer (d)] into the solution containing cation nature starch as an active principle.

[0014] It is under [solution / which contains cation nature starch 20 - 80 weight sections especially] setting. The (a) acrylamide and/or meta-acrylamide 40-98.5-mol % (b) anionic vinyl monomer 2-30.0-mol % (c) cross-linking vinyl monomer 0.02-10.0-mol % (d) cation nature vinyl monomer The additive for paper manufacture whose graft polymerization object obtained by carrying out the polymerization of the monomer mixture 80 which consists of 0-20.0-mol % - the 20 weight sections is an active principle is added to a raw material pulp slurry, as a conventional method paper making and by drying It has the outstanding tensile strength and the intensity in a layer, and is going to offer the additive for paper manufacture which can also hold a tearing strength stably on high level simultaneously.

[0015] In this invention, cation nature starch means the thing which made a kind of basic nitrogen chosen from the group which becomes starch, such as a zea, wheat, a potato, rice, and tapioca, from each

amino group of the 1st class, the 2nd class, and the 3rd class, and the 4th class ammonium contain at least. A certain thing of the content of basic nitrogen is desirable 0.3% of the weight or more, its 4th-class on-MONIUMU machine is the most desirable as basic nitrogen, and its tapioca starch is the most desirable as starch. Moreover, both the ionicity starch that introduced anionic machines (for example, phosphoric ester machine etc.) into the above-mentioned cation nature starch is also usable.

[0016] As an anionic vinyl monomer of this invention, an acrylic acid, a methacrylic acid, an itaconic acid, a maleic anhydride, a vinyl sulfonic acid, 2-acrylamide-isobutane sulfonic acids or those sodium salt, potassium salt, an ammonium salt, etc. are mentioned.

[0017] If a thing typical as a cross-linking vinyl monomer of this invention is illustrated As a methylol acrylamide, an N,N-dimethyl acrylamide, and screw (meta) acrylamides, as a methylene screw (meta) acrylamide, an ethylene screw (meta) acrylamide, and a 2 functionality vinyl monomer Ethylene glycol di(meth)acrylate diethylene-glycol di(meth)acrylate, Di(meth)acrylate, such as TOCHIECHIREN glycol di(meth)acrylate As divinyl ester, such as an adipic-acid divinyl sebacic-acid divinyl, epoxy acrylate, urethane acrylate, a divinylbenzene, and a 3 functionality monomer As 1.3.5 thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, triallyl trimellitate, an N,N-diaryl acrylamide, and a 4 functionality vinyl monomer Tetramethylolmethane tetraacrylate, tetrapod allyl-compound pyromellitate, etc. are mentioned.

[0018] As a cation nature vinyl monomer of this invention, the vinyl monomers which have the 3rd class amino groups, such as dimethylamino ethyl acrylate, dimethylaminoethyl methacrylate, diethylamino ethyl acrylate, diethylamino ethyl methacrylate, a dimethylamino propyl acrylamide, and a dimethylamino propyl meta-acrylamide, or those salts, quarternary ammonium salt, etc. can be illustrated.

[0019] Moreover, Nonion nature vinyl monomers, such as an acrylic ester in which these and copolymerization other than the above-mentioned composition monomer are possible (meta), styrene, and vinyl acetate, can also be used in the range which does not damage the effect of this invention substantially.

[0020] As a manufacturing method of the graft starch polymer of this invention, it can carry out by various well-known methods conventionally. For example, the cation nature starch solution which is the constituent of this invention, and said each monomer component (a), (b), (c), (d) and water are taught to the reaction container equipped with the agitator and the nitrogen gas introduction pipe. As a polymerization initiator, peroxides, such as a hydrogen peroxide, an ammonium persulfate, persulfuric-acid potash, and ammonium hydroperoxide, Or the arbitrary redox initiators which consist of combination of these peroxide and reducing agents, such as sodium bisulfite Furthermore, what is necessary is to use a water-soluble azo system initiator like 2,2'-azobis (2-amidinopropane) hydrochloric acids etc., to make it react with the reaction temperature of 40-80 degrees C for 1 to 5 hours, and just to obtain both the ionicity graft starch polymer.

[0021] When using N and N dimethyl acrylamide as a cross-linking vinyl monomer of this invention, it is necessary to add the radical catalyst of an oxidizing quality to the graft starch polymer containing N obtained by the above-mentioned polymerization method, and N dimethyl acrylamide, and to perform crosslinking reaction. As an oxidizing quality radical catalyst, organic peroxides, such as a hydrogen peroxide, the inorganic peroxides of persulfates (an ammonium persulfate, persulfuric-acid potash, etc.) and ketone peroxide, a peroxy ketal, hydroperoxide, diacyl peroxide, peroxy carbonate, and peroxy ester, etc. are mentioned. 0.1-1 mol of oxidizing quality radical catalysts is used to N and one mol of N dimethyl acrylamides.

[0022] Although the additive for paper manufacture of this invention is manufactured in the form of aqueous distribution liquid of about about 10 - 20 % of the weight of solid contents In case this is used for paper manufacture, 0.05 to 10% per pulp dry weight by solid-content conversion preferably It can add to raw material pulp in the amount which corresponds to 0.1 - 3%, and many intensity, such as tensile strength at the time of dryness of paper, intensity in a layer, and a tearing strength, can be improved by carrying out paper making as a conventional method, and drying.

[0023] Below, the example of the additive for paper manufacture of this invention, an application, and

the example of comparison are shown.

[0024] [Example 1] After preparing the mixed liquor of 150g [of cation nature tapioca starch (0.42% of nitrogen contents) solution of 18% of concentration cooked at 90-100 degrees C], and acrylamide 60g of 40% concentration, 3.4g of 80% concentration acrylic acids, and 150g of water to pH 4.0 using a caustic potash solution 10%, 0.4g is added for N and N dimethylacrylamide.

[0025] Next, added 2.7ml (APS) of ammonium-persulfate solution, and 2.7ml (SBS) of 2% sodium-bisulfite solution 2% at the temperature of 50 degrees C, it was made to react at the temperature of 60-80 degrees C for 3 hours, and the graft polymer was obtained.

[0026] Next, 4.4g of ammonium persulfates was added 10%, and it reacted at 70-80 degrees C for 4 hours, and after adding 80g of water, it adjusted to PHs 6-7 in caustic potash solution 10%, and both the ionicity graft starch polymer was obtained. The result is shown in Table 1.

[0027]

[Table 1]

	CS/モノマー 重量比	モノマー (組成 モル%)				P H 10倍液	固形分 %	粘 度 cps/25°C
		(a) 成分	(b) 成分	(c) 成分	(d) 成分			
実施例 1	50/50	AAM 89	AA 10	DMA 1	—	6. 4	1 2. 0	2600
2	50/50	AAM 86	AA 10	N-MAA 2	DMA PAA 2	7. 0	1 2. 0	2300
3	50/50	AAM 88	AA 10	N-MAA 2	—	6. 2	1 2. 5	4000
4	50/50	AAM94.95	AA 5	MBAA 0.05	—	6. 4	1 2. 4	3300
5	70/30	AAM 86	AA 3	N-MAA 4	DMA PAA 7	6. 5	1 2. 4	4500
比較例 1	50/50	AAM 90	AA 10	—	—	6. 4	1 2. 3	3000
2	70/30	AAM 90	AA 7	—	DMA PAA 3	6. 4	1 2. 4	3600
3	30/70	AAM 85	AA 10	—	※2HEA 5	6. 2	1 2. 1	2500

CS : 陽イオン性澱粉、AAM : アクリルアミド、DMA : N,N-ジメチルアクリルアミド、AA : アクリル酸、
N-MAA : N-メチロールアクリルアミド、DMA PAA : ジメチルアミノプロピルアクリルアミド、MBAA : メチレンビスアクリルアミド、
※2HEA : 2-ヒドロキシethylアクリレート (ノニオン性ビニルモノマー)

[Example 2] After preparing acrylamide 70g [of 197.5g of cation nature tapioca starch (0.42% of nitrogen contents) solution of 17% of concentration cooked at 90-100 degrees C, and 40% concentration], 4.1g [of 80% concentration acrylic acids], and dimethylamino propyl acrylamide 1.4g, and the mixed liquor of 180g of water to pH 4.0 using a caustic potash solution 10%, N-methylol acrylamide 0.9g is added. Next, add 2%APS2.5ml and 2%SBS2.5ml at the temperature of 50 degrees C, and it was made to react at the temperature of 60-80 degrees C for 3 hours, and after an appropriate time, it adjusted to PHs 6-7 in caustic potash solution 10% after adding 110g of additional water, and both the ionicity graft starch polymer was obtained. The result is shown in Table 1.

[Examples 3-5] In the example 2, the kind of (a) - (d) component or its combination composition (mol %) was changed, as shown in Table 1, and also both the ionicity graft starch polymer was obtained by

the same method as an example 2. The character is written together to Table 1.

[0028] [Examples 1-3 of comparison] In the example 2, the kind of (a) - (c) component or its combination composition (mol %) was changed, as shown in Table 1, and also both the ionicity graft starch polymer was obtained by the same method as an example 2. The character is written together to Table 1.

[0029] [Applications 1-5] Both the ionicity graft starch that added KOROPA-RU E-5 (a rosin system emulsion sizing compound and product made from 50%:Seiko Chemical Industries stock of concentration) by the weight for pulp, added the sulfuric-acid band 1.8% by the weight for pulp 0.15% to the pulp slurry of N-UKP (CSF530ml), and was subsequently previously obtained in the example (1-5) was added 0.5% by the weight for pulp, and it mixed enough. In this way, after pressing each obtained adjustment pulp slurry in paper equivalent to a basis weight 75/m² for 5 minutes by **** and 3.5 kg/cm² by TAPPI Standa-DOSHI-TOMASHIN, it dried for 1.5 minutes at 105 degrees C.

[0030] in this way, each obtained extract paper -- preparing -- quality of paper -- the examination was presented A test result is shown in Table 2.

[0031]

[Table 2]

	両イオン性 多糖重合体	坪 量 g/m ²	引張強度 kg	層内強度 (g)	比引裂き強度
実施応用例 1	実施例 1	76.2	8.7	145	135
2	2	75.8	8.9	145	132
3	3	75.7	8.6	145	133
4	4	75.8	8.3	140	133
5	5	75.9	8.7	150	130
比較応用例 1	比較例 1	75.5	7.7	125	133
2	2	75.4	7.3	120	135
3	3	76.0	8.3	135	130
参考例 1	スターガム A-15	75.6	8.3	120	100

[Comparison applications 1-3] Extract paper was obtained by the same operation as the aforementioned application except having used the examples 1-3 of comparison instead of both the ionicity graft starch polymer used by the application. this extract paper -- quality of paper -- it examined A result is written together to Table 2.

[0032] [Example 1 of reference] Instead of both the ionicity graft starch polymer used by the application, extract paper was obtained by the same operation as the aforementioned application except having used the star gum A-15 (an anionic acrylamide system paper reinforcing agent, product made from 15%: star photochemistry stock of concentration). this extract paper -- quality of paper -- it examined A result is written together to Table 2.

[0033] quality of paper -- it deals in a measuring method with a degree's, and comes out of it

[0034]

tensile strength (kg) : JIS P-8113 length hiatus intensity : JIS on-the-strength [in P-8116 layers]
(internal intensity of paper): -- edited by Japan Technical Association of the Pulp and Paper Industry
"the kind and the examining method of paper pulp" -- "the measuring method by the tensile-strength testing machine" of a 248-page publication -- conformity

[Translation done.]